Tetrahedron 68 (2012) 2052–2060

Contents lists available at SciVerse ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Four-coordinate organoboron compounds from β-enaminonitriles and diazonium salts

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ARTICLE INFO

Article history:
Received 7 October 2011
Received in revised form 20 December 2011
Accepted 29 December 2011
Available online 5 January 2012

Dedicated to Professor Josef Panchartek on occasion of his 80th birthday

Keywords:
Triazaborines
Enaminonitriles
Diazonium tetraphenylborate
Boron heterocycles

ABSTRACT

β-Enaminonitriles react with substituted benzenediazonium tetraphenylborates to form 1,2,4,3λ^4-triazaborines or 1,3,2λ^4-oxazaborines. The formation of either the first or the second product is affected by the reaction conditions, especially by the presence of water in the reaction components and in the solvent. If the reaction is performed under anhydrous conditions, the major product is the triazaborine. When 'wet' diazonium salts are used or a small amount of water is added into the reaction mixture, oxazaborine is the product.

1. Introduction

So-called polarized ethylenes, that is, compounds with their double bond substituted with a strongly electron-withdrawing group at the carbon C-1 and a strongly electron-donating group at the carbon C-2, represent, thanks to their versatile reactivity, important building blocks for the syntheses of a wide variety of different heterocyclic systems of practical usability (pharmaceuticals, fungicides and solvatochromic dyes[1]). β-Enaminonitriles (3-aminoalkenenitriles, Fig. 1), including 3-aminobut-2-enenitrile (Fig. 1, R^1=Me, R^2=H) and its *N*-substituted derivatives, belong among simple representatives of the polarized ethylenes. Enaminonitriles react with a number of reagents[1,2] to form substituted pyridines,[3] dihydropyridines,[3i,k,4] pyrazoles,[5] quinolines[4e,6] and other heterocyclic compounds.[5f,6,7]

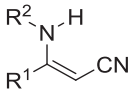

Fig. 1. The general structure of β-enaminonitriles.

There are very few mentions of the reactions of β-enaminonitriles with diazonium ions as an electrophilic reagent in the literature. The products of such reactions are azo or hydrazo compounds;[8] only one work mentions the formation of a heterocyclic compound.[9]

The aim of this work is to study the reaction of β-enaminonitriles with substituted benzenediazonium tetraphenylborates. In this way it is possible to prepare new heterocyclic compounds, oxazaborines and triazaborines with four-coordinate boron atoms (an arrangement of the heteroatoms in the cycles N–B(Ph$_2$)–O and N–B(Ph$_2$)–N–N).

Various kinds of heterocyclic compounds containing boron atoms in their molecules are interesting in terms of their photophysical and electrochemical properties and biological activity,[10] by which they differ substantially from their carbocyclic analogues. The properties of chiral compounds containing the (Ph$_2$)B group have also been studied.[11] Four-coordinate boron compounds having two phenyl groups adjacent to boron are interesting with regard to their potential photoluminescent and electroluminescent properties[12] and are potentially available as materials for organic light-emitting diodes (OLEDs). Some of them undergo reversible photochromic switching[13] or can show NLO properties.[14]

In our previous works we described a new preparation of polysubstituted oxazaborines, diazaborines and triazaborines by the reaction of diazonium tetraphenylborates with β-enaminones and

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doi:10.1016/j.tet.2011.12.082

β-enaminoamides.[15] All the compounds prepared by means of the method contain the structural motif $-(Ph_2)B^{-}-N^{+}-$. This reaction, described by us, enables both preparation of the compounds with various combinations of substituents and modification of the substituents already present on them to be conducted to achieve the desired properties.

2. Results and discussion

One of the first mentions of the reactions of β-enaminonitriles with diazonium salt is from 1964. The reaction was performed in aqueous pyridine and, according to the authors, the products were mixtures of azo/hydrazono tautomers.[8d,e] This assumption, however, has not been confirmed experimentally.

According to the literature, the reactions of β-enaminonitriles have been studied hitherto in protic environments only and under such conditions that hydrolysis of either the starting nitriles or the primarily formed products of the azo coupling took place to give 2-arylhydrazono-3-oxobutanenitriles.[8f,g] 3-Amino-2-phenyldiazenyl-3-phenyl-prop-2-enenitrile or its imino-phenylhydrazono tautomer, respectively, that is, the real product of the azo coupling to β-enaminonitrile, was prepared by another method: the reaction of phenylmagnesium bromide with 2-phenylhydrazonopropanedinitrile.[16] The tautomeric form of the compound was not determined. By means of the reaction of β-enaminonitriles with diazonium tetrafluoroborates[17] or tetraphenylborates in dichloromethane in the presence of remelted sodium acetate it is possible to prepare the products of the azo coupling without the risk of hydrolysis of the enamino group. We found that the products of the azo coupling prepared in this way are a mixture of two isomers, which differ with regard to the existence of an intramolecular hydrogen bonding.

The azo coupling product **5a** exists in DMSO-d_6 solution as a mixture of two *E*/*Z* isomers (Fig. 2). The ratio of the isomers was estimated on the basis of ^{1}H NMR data and was found to be 1:0.37. To distinguish between the isomers, selectively ^{15}N enriched isotopomer was prepared and the stereochemical significance of ^{13}C–^{15}N coupling constants was used.

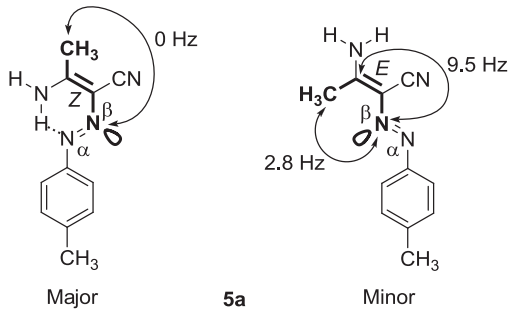


Fig. 2. Geometric isomers of the compound **5a**.

The geminal coupling constant ^2J (^{13}C, ^{15}N) for C3 is observable only in the minor form, having a relatively large value, 9.5 Hz. It corresponds to the *syn* arrangement of the nitrogen lone pair relative to the carbon C3, which evidences that the minor form is the *E* isomer (Fig. 2; minor).[18] The value of the coupling constant ^3J (^{13}C, ^{15}N) is 2.8 Hz for the minor form, whereas no splitting was observed for the major form. This is also in agreement with the minor form being an *E*-isomer because the *anti* arrangement of C and N with the orientation of the electron lone pair, as shown in Fig. 2 (**5a**, major form), has a lower value of the coupling constant ^3J (^{13}C, ^{15}N) than any *syn* arrangement.[18]

^{15}N Chemical shifts of both the forms correspond to the practically pure azo form. The position of the tautomeric equilibrium is then analogical as in the case of the enamino ketones[17] and opposite to the products of the azo coupling to propanedinitrile, methyl cyanoacetate,[19] ethyl 3-oxobutanoate, pentane-2,4-dione, or dimethyl propanedioate, which exist as pure hydrazo forms.[20]

Upon reaction of 3-aminobut-2-enenitrile with 4-methylbenzenediazonium tetraphenylborate (dried in air) in dry dichloromethane, a mixture of compounds is formed (according to TLC). 6-Amino-4-methyl-5-(4-methylphenyldiazenyl)-2,2-diphenyl-3*H*-1,3, 2λ^4-oxazaborine (**4a**) was isolated from the mixture by means of column chromatography, with a yield of 30% (after crystallization). The compound was identified on the basis of ^{1}H, ^{15}N and ^{11}B NMR spectra.

From the ^{1}H NMR spectrum (Fig. 3) it is clear that the product has three acidic hydrogens. All belong to N–H groups, which was proved by reading the coupling constants ^1J (^{15}N, ^{1}H) from 0.18% ^{15}N satellites in the proton spectrum as well as by measuring the 1D ^{1}H–^{15}N *gs*HMBC NMR spectrum (Fig. 4). The values of these three coupling constants are $^1J_{N-H}$=90.3, 81.5 and 94.4 Hz. The chemical shifts of the nitrogen atoms are shown in Table 1. Positive values of δ (^{15}N), 22.2 and 86.4, correspond to the presence of an azo group.[17a,21] The value of the ^{11}B chemical shift corresponds to the values obtained for six-membered heterocyclic compounds with an N–B–O arrangement.[15] The structure of the oxazaborine **4a** was subsequently confirmed by X-ray analysis. ORTEP plot is shown in Figs. 5 and 6.

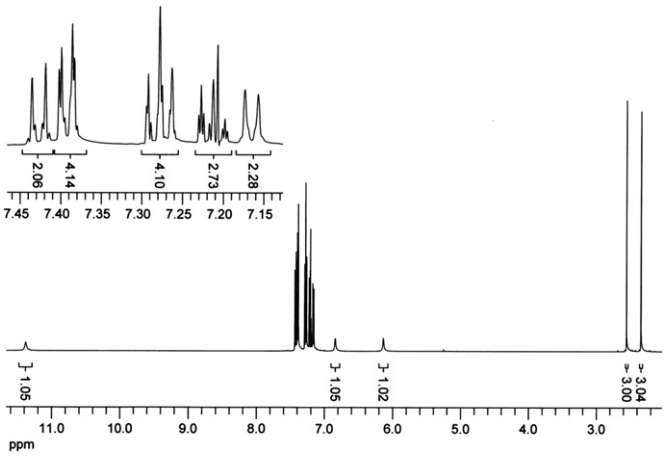


Fig. 3. 500 MHz ^{1}H NMR spectrum of **4a** in $CDCl_3$.

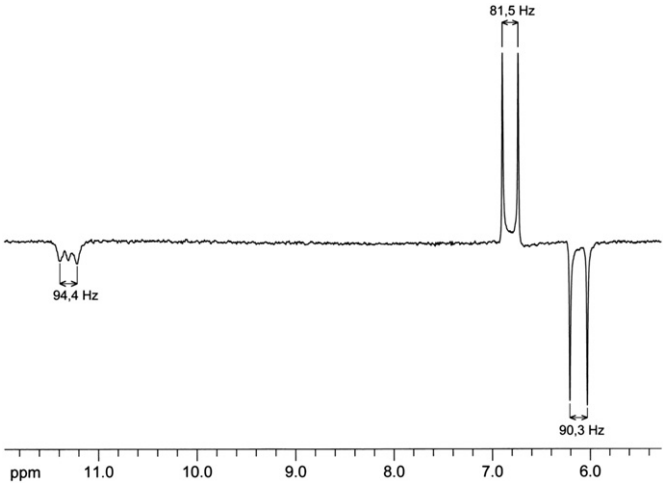


Fig. 4. 1D ^{1}H–^{15}N *gs*HMBC NMR spectrum of the compound **4a** in $CDCl_3$.

Table 1
^{15}N and ^{11}B chemical shifts of compounds **3a**–**f** and **4** in $CDCl_3$ (For notation of nitrogen see Scheme 1)

Product	$^{15}N1$	$^{15}N2$	$^{15}N3$		^{11}B
3a[a]	−141.9	25.5	−204.2	−168.3 (CN)	−1.2
3b	−148.3	21.2	−202.1		1.26
3c[b]	−137.4	31.8	−214.9		−1.11
3d	−145.6		−206.0		1.16
3e[c]	−141.3		−207.5		−0.99
3f	−148.0	20.2	−203.7		1.01
3g[d]	−137.1		−217.1		−0.94
3h	−145.0		−207.8		0.94
3i[e]	−142.9		−203.9	−176.7 (CN)	−1.02
3j[f]	−136.7		−211.8	−186.2 (CN)	−1.14
				−330.6 (NMe2)	
4a[g]	22.2	86.4	−222.3	−277.9 (NH2)	2.12
4b	21.1	82.3	−223.5		1.99
4c[h]	27.5		−225.3	−276.3 (NH2)	2.19

[a] ^1J ($^{15}N3$, ^1H)=83.2 Hz.
[b] ^1J ($^{15}N3$, ^1H)=83.5 Hz.
[c] ^1J ($^{15}N3$, ^1H)=82.6 Hz.
[d] ^1J ($^{15}N3$, ^1H)=82.5 Hz.
[e] ^1J ($^{15}N3$, ^1H)=81.8 Hz.
[f] ^1J ($^{15}N3$, ^1H)=81.7 Hz.
[g] ^1J ($^{15}N3$, ^1H)=81.3 Hz, ^1J ($^{15}N4$, ^1H)=89.5 Hz, ^1J ($^{15}N4$, ^1H)=90.8 Hz.
[h] ^1J ($^{15}N3$, ^1H)=81.6 Hz, ^1J ($^{15}N4$, ^1H)=89.6 Hz, ^1J ($^{15}N4$, ^1H)=90.7 Hz.

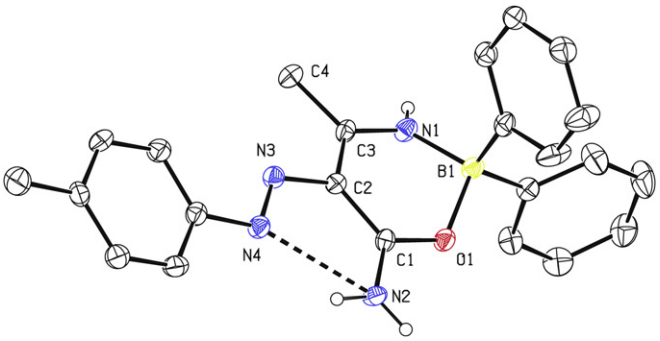


Fig. 5. ORTEP view of oxazaborine **4a** displaying the thermal ellipsoids at 30% probability; hydrogen atoms, except those involved in hydrogen bonds, are omitted for clarity.

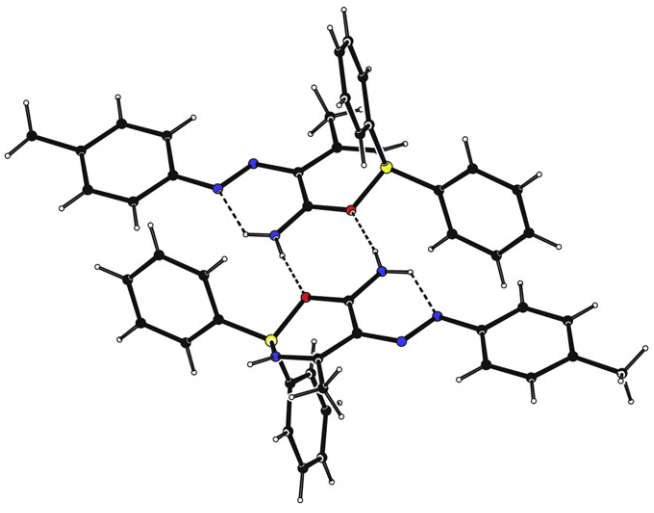


Fig. 6. Chain of hydrogen bonded molecules in crystal packing of oxazaborine **4a**.

By modification of the reaction conditions ($CH_2Cl_2/Et_2O/H_2O$ in ratio 30:10:0.3, vol, under reflux) the yield of the oxazaborine **4a** increased up to 45%.

If the diazonium salt was dried for about 1 h in vacuo at room temperature before being added to the reaction mixture, the major product was triazaborine **3a** (Scheme 1). The reaction was initially performed in dichloromethane at room temperature for 72 h. The yield was 48% after chromatography and crystallization. When the reaction was carried out in dichloromethane/toluene mixture (3:5 v/v) under reflux, shortening of the reaction time to 3 h was achieved. The yield was comparable (Table 2).

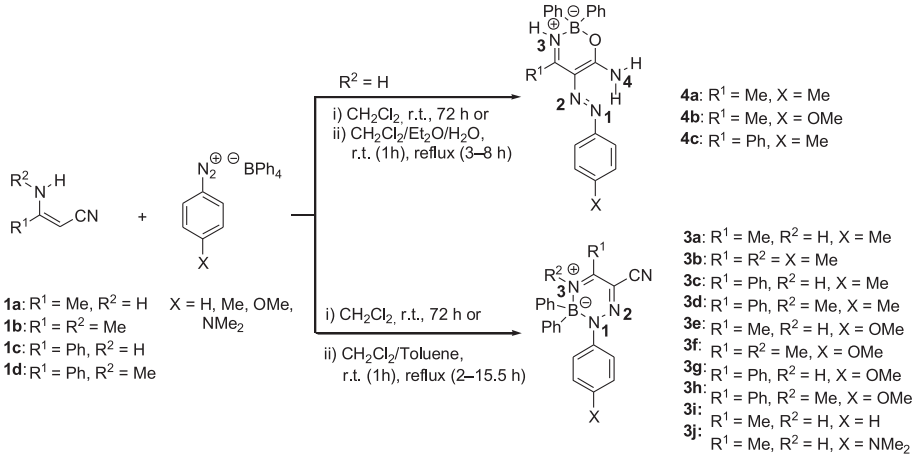
The reaction leading to the triazaborines proceeds with enaminonitriles both with a primary amino group and with an *N*-methyl group (Scheme 1). When the enaminone **1e** with an *N*-phenyl group was used, no heterocyclic compound was obtained but the azo coupling product **5b** only (Scheme 2).

We have suggested a possible mechanism of formation of the oxazaborines (Scheme 3). We assumed that in situ formation of diphenylborinic acid and its subsequent reaction with the azo coupling product **5a** at amino group nitrogen took place. To be able to confirm the mechanism, we experimented with preparing the compound **4a** independently. We prepared 3-amino-2-(4-methylphenyldiazenyl)but-2-enenitrile by the azo coupling reaction and left it to react with freshly prepared diphenylborinic acid (Scheme 4). However, according to NMR spectra, the product was not the oxazaborine **4a** but the triazaborine **3a**. This was then confirmed by means of X-ray diffraction (Fig. 10). Hence, the oxazaborines are not formed according to the suggested mechanism (Scheme 3).

Nitriles react with a number of Lewis acids.[22] Upon coordination of a Lewis acid on the electron lone pair of nitrogen of the nitrile group, an increase in the polarity of the group takes place. Subsequent addition of water to form amide is then accelerated by several orders of magnitude. From the literature[23] nitriles are known to form coordination compounds $R-C\equiv N^+-{}^-BPh_3$ with triphenylborane. Triphenylborane is formed in the course of the reaction of diazonium tetraphenylborate with protons introduced during azo couplings to polarized ethylenes (Scheme 3).[15a] After coordination of the triphenylborane with the $-C\equiv N$ nitrogen, the addition of water, present in a small amount, can easily take place to form amide. The isolated oxazaborines **4** (Figs. 5–8) are then probably formed not directly from enaminonitriles but from their hydration products (Scheme 3). The oxazaborines are really formed as the main products from enaminoamides.[15b]

The reaction of the enaminonitriles with diazonium tetraphenylborates to give triazaborines probably proceeds by the same mechanism as we have suggested before for other polarized ethylenes.[15] In the case of enaminones it was possible to prove (by means of NMR experiments) that the reaction goes through a non-isolable intermediate, hydrazone $\mathbf{Im_a}$ (Ref. 15a, Fig. 9). The formation of an analogous intermediate $\mathbf{Im_b}$ was observed for the enaminonitriles, as well. It was possible to isolate the intermediate if the reaction was done at room temperature in dichloromethane. The intermediate $\mathbf{Im_b}$ was cyclized in toluene under reflux to the triazaborine **3a**.

The intermediate $\mathbf{Im_b}$ was, in the case of the reaction of 3-aminobut-2-enenitrile with 4-methylbenzenediazonium tetraphenylborate, identified on the basis of comparison of its ^{13}C chemical shifts with those of the major isomer of 3-amino-2-(4-methylphenyldiazenyl)but-2-enenitrile (for the part of the intermediate $\mathbf{Im_b}$ coming from the enaminonitrile and the diazonium ion) and a hitherto unpublished ^{13}C NMR spectrum of the isolated coordination compound of triphenylborane with ethyl 3-amino-2-(4-methylphenyl-hydrazono)butanoate[24] (for the part of the molecule containing the Ph_3B^- group). The ^{13}C spectrum, combined in this manner, is practically identical with the spectrum of the intermediate $\mathbf{Im_b}$ (Table S1). It was not possible to purify the compound for microanalysis due to its cyclization when crystallization

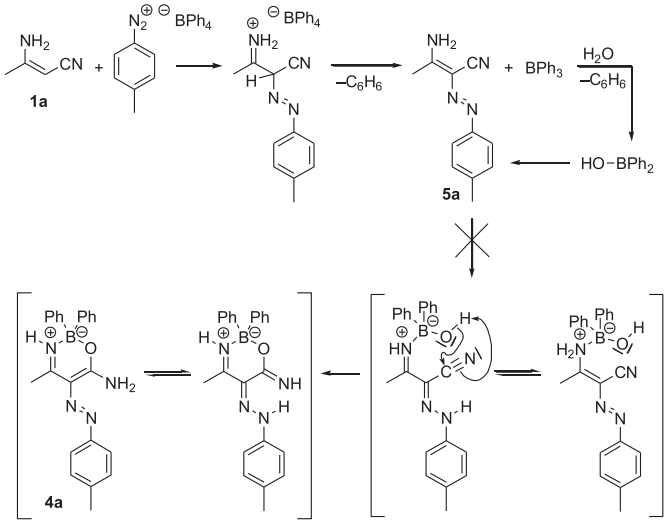


Scheme 1. Reaction of β-enaminonitriles **1** and 4-substituted benzenediazonium tetraphenylborate.

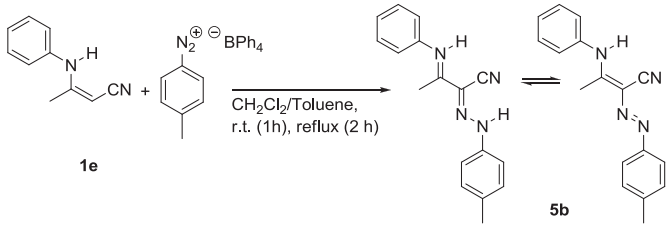
Table 2
Reaction conditions and yields for reaction of **1a**–**e** with diazonium salts

Product	Solvent[a]	Temperature	Time (h)	Yield[b] (%)	Yield[c] (%)
3a	CH_2Cl_2[a]	rt	1	Traces	—
3a	CH_2Cl_2[a]	rt	72	76	48
3a	CH_2Cl_2/toluene	Reflux	3	72	53
3b	CH_2Cl_2/toluene	Reflux	3	63	49
3c	CH_2Cl_2/toluene	Reflux	3	75	60
3d	CH_2Cl_2/toluene	Reflux	4	55	35
3e	CH_2Cl_2/toluene	Reflux	3	85	62
3f	CH_2Cl_2/toluene	Reflux	15.5	60	47
3g	CH_2Cl_2/toluene	Reflux	1.5	80	62
3h	CH_2Cl_2/toluene	Reflux	3	65	40
3i	CH_2Cl_2[a]	rt	72	70	50
3i	CH_2Cl_2/toluene	Reflux	2	74	50
3j	CH_2Cl_2/toluene	Reflux	4.5	42	30
5b	CH_2Cl_2/toluene	Reflux	2	61	51
4a	CH_2Cl_2[a]	rt	72	—	30
4a	CH_2Cl_2/Et_2O/H_2O	Reflux	4	—	45
4b	CH_2Cl_2/Et_2O/H_2O	Reflux	3	—	21
4c	CH_2Cl_2[a]	rt	72	—	24

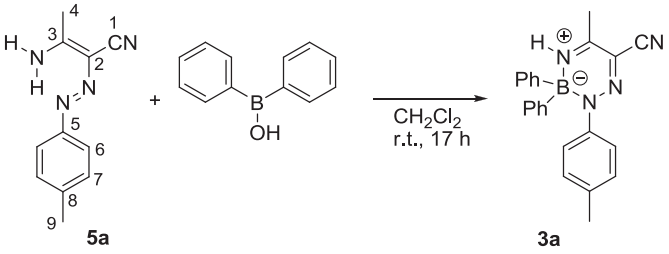
[a] Dichloromethane was used (35 mL/5 mmol).
[b] Isolated yield (after column chromatography).
[c] Yield after recrystallization.



Scheme 3. The proposed (and finally rejected) mechanism for preparation of oxazaborines **4** from diphenylborinic acid.



Scheme 2. Reaction of β-enaminonitrile **1e** and 4-methylbenzenediazonium tetraphenylborate in mixture of CH_2Cl_2/toluene at reflux.



Scheme 4. Reaction of azo compound **5a** with diphenylborinic acid in CH_2Cl_2 at room temperature.

was attempted. The structure of the intermediate $\mathbf{Im_b}$ was confirmed by means of HRMS.

ORTEP views of the compounds **3a**, **3h**, **3j**, **4a** and **4b** are shown in Figs. 5–8,10–14. The oxazaborines **4a** and **4b** display intramolecular short N–H···N resonance assisted hydrogen bonds[25] (Table S3) between the enamino and the diazenyl group.[15b,17d] The HN2–C1=C2–N3=N4 heterodienic systems exhibit extended conjugation within the C2=C1–N2–H enamino moiety and weaker delocalisation within the C2–N3=N4 diazenyl one. In both the compounds **4a** and **4b** the N–H groups are not involved in any intermolecular H-bond. The triazaborines **3h** and **3j** exhibit the HN1=C2–C1=N3 (HN5D=C48–C47=N7 and HN9D=C25–C24=N11 for **3a**) heterodienic systems display a good delocalisation within the cyano groups. Triazaborines **3a**, **3h** and **3j** contain the cyano substituent at C1 for **3h** and **3j**, and, C47 and C24 for **3a**, respectively, which forms the usual intermolecular N–H···NC (for **3a**) hydrogen bonded chain, but rather unusual N1–H1···C6*i* (*i*=½–*x*, ½+*y*, ½–*z*) intermolecular connection between the amino group and the aromatic system from adjacent molecule, as a short

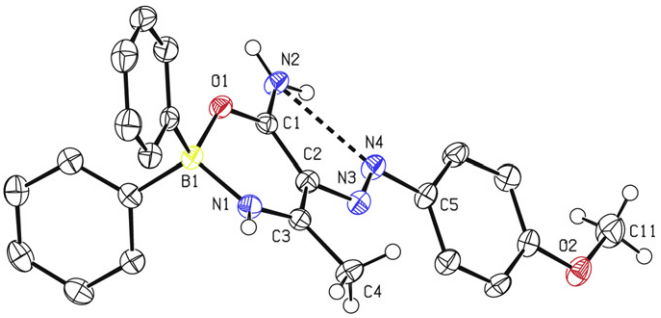


Fig. 7. ORTEP view of oxazaborine **4b** displaying the thermal ellipsoids at 50% probability; some hydrogen atoms are omitted for clarity.

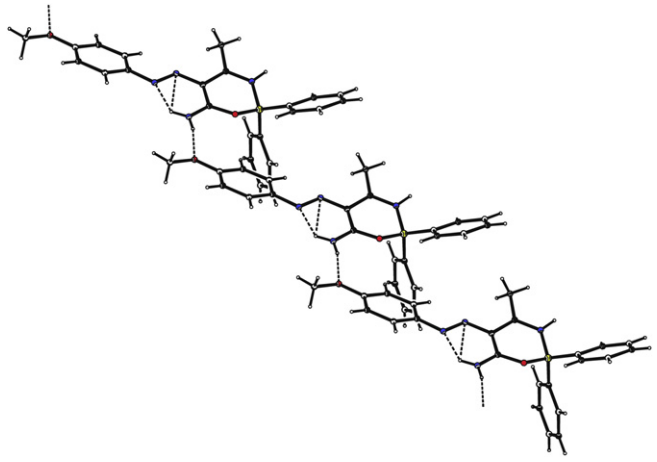


Fig. 8. Chain of hydrogen bonded molecules in crystal packing of oxazaborine **4b**.

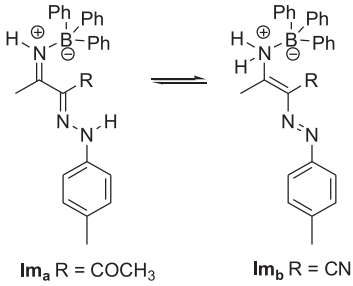


Fig. 9. The structure of intermediate on the route to triazaborines.

intramolecular contact. The six boron heterocycles assume quite similar conformations, as evidenced by the puckering parameters[26] in Table S4.

3. Conclusion

By means of the reaction of β-enaminonitriles with substituted benzenediazonium tetraphenylborates in the absence of water, substituted triazaborines were formed. If water was present in the reaction mixture, oxazaborines, which formed after hydrolysis of the nitrile group in one of the reaction stages, were the major products. If the amino group of the starting β-enaminonitrile was substituted with the phenyl group, only the azo coupling product was isolated. The compounds were characterized by means of NMR spectroscopy (^{1}H, ^{13}C, ^{15}N and ^{11}B, see Table 1 and Experimental section) and some were also characterized by means of X-ray diffraction.

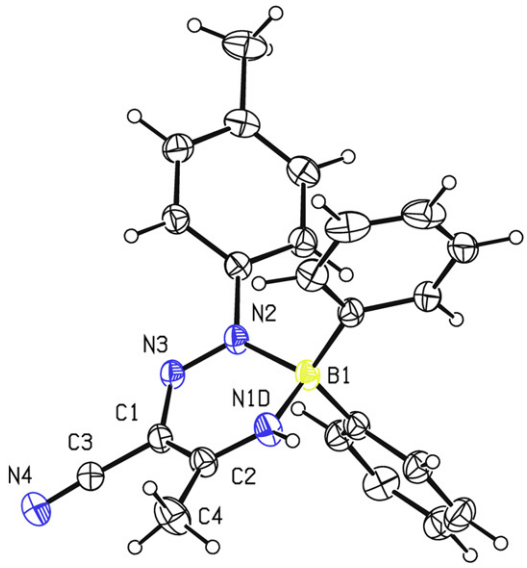


Fig. 10. ORTEP view of triazaborine **3a** displaying the thermal ellipsoids at 50% probability.

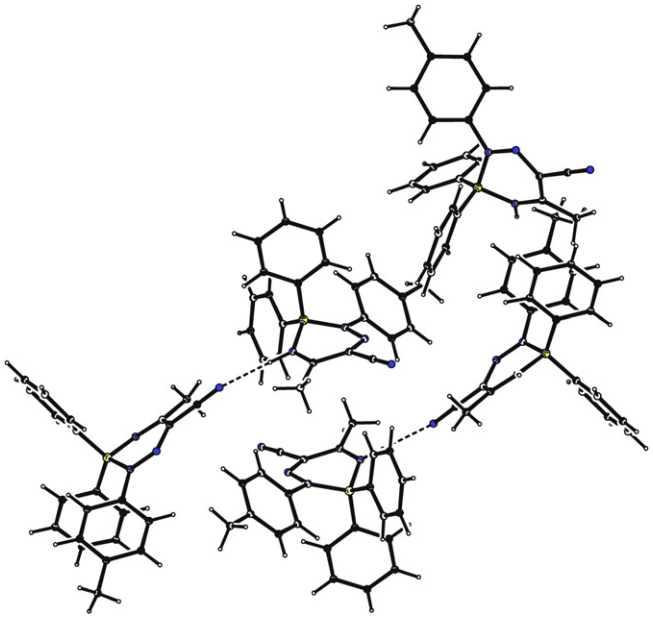


Fig. 11. Chain of hydrogen bonded molecules in crystal packing of triazaborine **3a**.

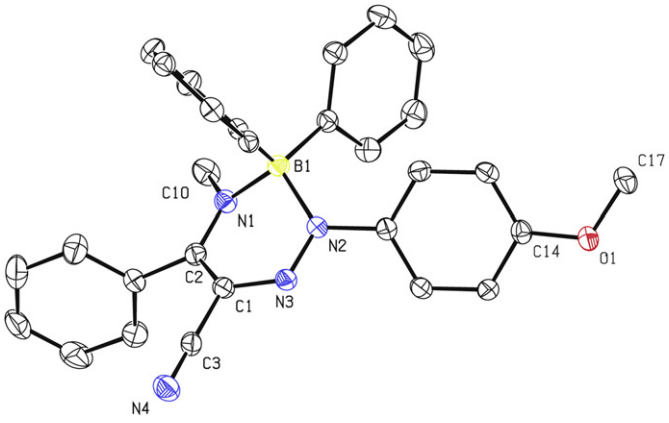


Fig. 12. ORTEP view of triazaborine **3h** displaying the thermal ellipsoids at 50% probability; hydrogen atoms are omitted for clarity.

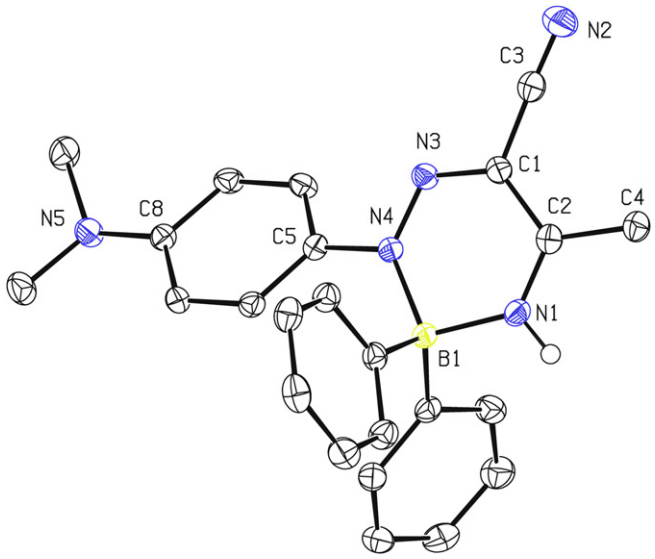


Fig. 13. ORTEP view of triazaborine **3j** displaying the thermal ellipsoids at 40% probability; hydrogen atoms, except those involved in hydrogen bonds, are omitted for clarity.

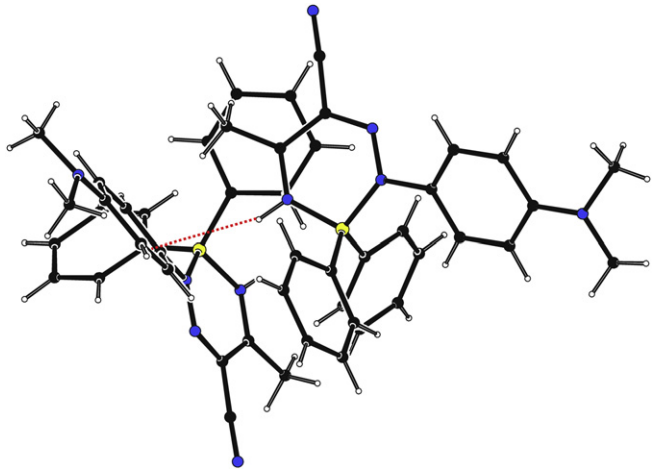


Fig. 14. Chain of hydrogen bonded molecules in crystal packing of triazaborine **3j**.

4. Experimental section

4.1. General

NMR spectra were measured at room temperature using a Bruker AVANCE 500 spectrometer equipped with a 5 mm broadband probe with a gradient of magnetic field in the direction of *z* axis operating at the frequencies 500.13 MHz (^{1}H), 125.77 MHz (^{13}C), 50.69 MHz (^{15}N) and a Bruker AVANCE III 400 operating at 400.13 MHz (^{1}H), 100.62 MHz (^{13}C), 128.38 MHz (^{11}B) and 40.55 MHz (^{15}N). The ^{1}H NMR spectra were calibrated in $CDCl_3$ on internal standard (hexamethyldisiloxane (δ 0.05) or tetramethylsilane (δ 0.00)) and the ^{13}C NMR spectra were calibrated on the central signal of the solvent multiplet (δ 76.9). The ^{13}C NMR spectra were measured in standard way and by means of the APT pulse sequence (spectral width 26.455 kHz, acquisition time 1.238 s, zero filling to 64 K and line broadening 1 Hz prior Fourier transformation). The ^{15}N NMR spectra were calibrated on external neat ^{15}N nitromethane placed in a coaxial capillary (δ 0.0). The δ (^{15}N) values were measured with the help of techniques with inversion detection (gradient selected 2D ^{1}H–^{15}N HMBC) processed in the magnitude mode. The gradient ratios were 70:30:50.1. Experiments were performed with the NH one-bond coupling 90 Hz, and NH long-range coupling 5 Hz, 2 K×160 zero filled to 2 K×1 K, sinebell squared in both dimensions. The ^{11}B NMR spectra were calibrated on external $B(OCH_3)_3$ placed in a coaxial capillary (δ 18.1). In order to suppress the signals of ^{11}B nuclei from NMR tube glass, the measurements were carried out in Teflon sample tube liners (Aldrich) inserted into 5 mm tubes whose bottom part of about 25 mm length was cut off.

The X-ray data for crystals of **3a**, **3h**, **3j**, **4a** and **4b** were obtained at 150 K using Oxford Cryostream low-temperature device on a Nonius Kappa CCD diffractometer with Mo Kα radiation (λ=0.71073 Å), a graphite monochromator, and the ϕ and χ scan mode. Data reductions were performed with DENZO-SMN.[27] The absorption was corrected by integration methods.[28] Structures were solved by direct methods (Sir92)[29] and refined by full matrix least-square based on F^2 (SHELXL97).[30] Hydrogen atoms were mostly localized on a difference Fourier map, however to ensure uniformity of treatment of crystal, all hydrogen were recalculated into idealized positions (riding model) and assigned temperature factors $H_{iso}(H)$=1.2 U_{eq} (pivot atom) or of 1.5 U_{eq} for the methyl moiety with C–H=0.96 Å and 0.93 Å for methyl and hydrogen atoms in aromatic ring, respectively, and 0.86 Å for N–H bonds. $R_{int}=\Sigma|F_o^2-F_{o,mean}^2|/\Sigma F_o^2$, $GOF=[\Sigma(w(F_o^2-F_c^2)^2)/(N_{diffrs}-N_{params})]^{1/2}$ for all data, $R(F)=\Sigma||F_o|-|F_c||/\Sigma|F_o|$ for observed data, $wR(F^2)=[\Sigma(w(F_o^2-F_c^2)^2)/(\Sigma w(F_o^2)^2)]^{1/2}$ for all data.

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 779055–779059 for **3a**, **3h**, **3j**, **4a** and **4b**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

HRMS spectrum was measured with ESI technique under negative ionization mode using LTQ Orbitrap Velos (Thermo Scientific) instrument.

Melting points were determined with a Kofler hot stage microscope and were not corrected. The microanalyses were carried out with a FISONS EA 1108 automatic analyser.

4.2. Starting compounds

Anhydrous dichloromethane was purchased commercially (Fluka) and distilled from P_2O_5 before use. Toluene and diethylether were dried over sodium. 3-Aminobut-2-enenitrile (**1a**) was purchased from Aldrich and crystallized from ethyl acetate. 3-Methylaminobut-2-enenitrile[31] (**1b**), 3-amino-3-phenylprop-2-enenitrile[32] (**1c**) and 3-phenylaminobut-2-enenitrile[31] (**1e**) was prepared as previously reported.

*4.2.1. 3-Methylamino-3-phenylprop-2-enenitrile (**1d**).* Methylamine (32 mL, 33% ethanolic solution) was added to solution of 3-oxo-3-phenylpropanenitrile[33] (4.05 g, 28 mmol) in ethanol (55 mL). The reaction mixture was heated to reflux and stirred 10 h at the same temperature. Ethanol was evaporated and dark yellow viscous oil was obtained. The oil was refluxed with charcoal (0.5 g) and methanol (20 mL). Then the mixture was filtrated and methanol was evaporated. Yield of the title compound was 3.1 g (70%). ^{1}H NMR spectrum was in accordance with that reported in Ref. 34.

4.2.2. Substituted benzenediazonium tetraphenylborates. Aniline or 4-substituted aniline (6.84 mmol) was dissolved in boiling aqueous hydrochloric acid (3 mL, 1:1). The solution was cooled to −5 °C and diazotised by gradual addition of a cold solution of sodium nitrite (0.49 g, 7.11 mmol) in water (1.5 mL). The temperature during the diazotation was maintained between −5 and 0 °C. The excess of nitrous acid (presence tested by starch-iodide paper) was

decomposed using the required amount of sulfamic acid. A solution of sodium tetraphenylborate (6.84 mmol) in water (75 mL) was added at once. The precipitated diazonium salt was filtered and washed with cold ethanol (1×30 mL) and diethylether (1×30 mL). The diazonium salts were prepared immediately before use and dried in vacuo at room temperature in a desiccator for about 1 h (CAUTION: dry diazonium tetraphenylborates can undergo violent decomposition when the crystalline material is ground!). The yields of diazonium salts were about 79–87%.

4.3. General procedure for reaction of 1a–e with 4-substituted benzenediazonium tetraphenylborates

To a cold (5 °C) solution of β-enaminonitriles **1a**–**e** (5 mmol) in dry dichloromethane (15 mL) and toluene (25 mL, dried over sodium) was added freshly prepared corresponding benzenediazonium tetraphenylborate (5 mmol). The reaction mixture was stirred 1 h at room temperature and then 2–15.5 h at reflux (See Table 2). The reaction mixture was cooled to room temperature and solvents were evaporated. The crude residue was chromatographed on silica gel with dichloromethane to give compounds **3a**–**3j** and **5b**.

*4.3.1. 5-Methyl-2-(4-methylphenyl)-3,3-diphenyl-4H-1,2,4,3λ^4-triazaborine-6-carbonitrile (**3a**).* Recrystallization from cyclohexane. Yield 0.97 g (53%), yellow crystals, mp 187–189 °C; [found: C, 75.74; H, 6.09; N, 15.23. $C_{23}H_{21}BN_4$ requires C, 75.84; H, 5.81; N 15.38%]. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.19 (s, 3H), 2.22 (s, 3H), 6.83–6.84 (m, 2H), 7.13–7.21 (m, 8H), 7.32–7.34 (m, 4H), 7.67 (br s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 20.7, 20.9, 110.0, 116.9, 122.7, 126.7, 127.3, 128.4, 133.2, 137.5, 144.5, 145.9 (br), 157.7.

*4.3.2. 4,5-Dimethyl-2-(4-methylphenyl)-3,3-diphenyl-1,2,4,3λ^4-triazaborine-6-carbonitrile (**3b**).* Recrystallization from cyclohexane. Yield 0.93 g (49%), orange crystals, mp 194–197 °C; [found: C, 76.28; H, 6.27; N, 14.69. $C_{24}H_{23}BN_4$ requires C, 76.20; H, 6.13; N 14.81%]. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.15 (s, 3H), 2.30 (s, 3H), 2.94 (s, 3H), 6.80–6.82 (m, 2H), 7.05–7.07 (m, 2H), 7.18–7.26 (m, 6H), 7.37–7.39 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 17.6, 20.7, 38.5, 111.1, 117.5, 122.9, 126.8, 127.5, 128.2, 133.6, 136.8, 144.1 (br), 144.8, 157.6.

*4.3.3. 2-(4-Methylphenyl)-3,3,5-triphenyl-4H-1,2,4,3λ^4-triazaborine-6-carbonitrile (**3c**).* Recrystallization from cyclohexane. Yield 1.28 g (60%), orange crystals, mp 219–222 °C. [found: C, 78.84; H, 5.71; N, 12.88. $C_{28}H_{23}BN_4$ requires C, 78.88; H, 5.44; N 13.14%]. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.22 (s, 3H), 6.92–6.94 (m, 2H), 7.19 (br s, 1H), 7.20–7.26 (m, 6H), 7.29–7.32 (m, 2H), 7.35–7.37 (m, 4H), 7.46–7.49 (m, 2H), 7.55–7.58 (m, 1H), 7.66–7.68 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 20.9, 110.0, 117.1, 123.4, 126.9, 127.5, 128.5, 128.6, 129.2, 130.9, 133.0, 133.3, 138.1, 144.6, 145.8 (br), 156.3.

*4.3.4. 4-Methyl-2-(4-methylphenyl)-3,3,5-triphenyl-1,2,4,3λ^4-triazaborine-6-carbonitrile (**3d**).* Recrystallization from toluene. Yield 0.78 g (35%), orange crystals, mp 262–264 °C; [found: C, 79.33; H, 5.95; N, 12.57. $C_{29}H_{25}BN_4$ requires C, 79.10; H, 5.72; N 12.72%]. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.20 (s, 3H), 2.81 (s, 3H), 6.87–6.89 (m, 2H), 7.14–7.16 (m, 2H), 7.22–7.25 (m, 2H), 7.26–7.32 (m, 6H), 7.42–7.44 (m, 4H), 7.50–7.51 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 20.8, 40.3, 111.7, 117.1, 123.4, 126.8, 127.2, 127.5, 128.3, 129.2, 130.6, 131.0, 133.7, 137.2, 143.9 (br), 144.9, 158.9.

*4.3.5. 2-(4-Methoxyphenyl)-5-methyl-3,3-diphenyl-4H-1,2,4,3λ^4-triazaborine-6-carbonitrile (**3e**).* Recrystallization from cyclohexane/toluene mixture. Yield 1.17 g (62%), yellow crystals, mp 180–182.5 °C; [found: C, 72.73; H, 5.84; N, 14.48. $C_{23}H_{21}BN_4O$ requires C, 72.65; H, 5.57; N 14.73%]. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.17 (s, 3H), 3.62 (s, 3H), 6.54–6.57 (m, 2H), 7.15–7.22 (m, 6H), 7.25–7.27 (m, 2H), 7.31–7.33 (m, 4H), 7.49 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 20.4, 55.1, 109.8, 112.9, 117.0, 124.3, 126.7, 127.4, 133.2, 140.5, 145.9 (br), 157.5, 158.7.

*4.3.6. 2-(4-Methoxyphenyl)-4,5-dimethyl-3,3-diphenyl-1,2,4,3λ^4-triazaborine-6-carbonitrile (**3f**).* Recrystallization from cyclohexane/toluene mixture. Yield 0.92 g (47%), orange crystals, mp 177–179 °C; [found: C, 73.09; H, 6.00; N, 14.01. $C_{24}H_{23}BN_4O$ requires C, 73.11; H, 5.88; N 14.21%]. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.24 (s, 3H), 2.90 (s, 3H), 3.56 (s, 3H), 6.46–6.49 (m, 2H), 7.08–7.11 (m, 2H), 7.15–7.18 (m, 2H), 7.20–7.24 (m, 4H), 7.36–7.38 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 17.4, 38.4, 54.9, 110.7, 112.6, 117.5, 124.3, 126.6, 127.4, 133.5, 140.6, 144.0 (br), 157.4, 158.1.

*4.3.7. 2-(4-Methoxyphenyl)-3,3,5-triphenyl-4H-1,2,4,3λ^4-triazaborine-6-carbonitrile (**3g**).* Recrystallization from toluene. Yield 1.37 g (62%), orange crystals, mp 226–229 °C; [found: C, 76.26; H, 5.50; N, 12.38. $C_{28}H_{23}BN_4O$ requires C, 76.03; H, 5.24; N 12.67%]. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.70 (s, 3H), 6.63–6.66 (m, 2H), 7.07 (br s, 1H), 7.21–7.27 (m, 6H), 7.35–7.38 (m, 6H), 7.49–7.52 (m, 2H), 7.58–7.61 (m, 1H), 7.69–7.70 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.2, 109.8, 113.1, 117.3, 125.0, 126.9, 127.5, 128.6, 129.2, 131.0, 133.0, 133.3, 140.6, 145.7 (br), 156.1, 159.2.

*4.3.8. 2-(4-Methoxyphenyl)-4-methyl-3,3,5-triphenyl-1,2,4,3λ^4-triazaborine-6-carbonitrile (**3h**).* Recrystallization from toluene. Yield 0.92 g (40%), orange crystals, mp 228–231 °C; [found: C, 76.44; H, 5.73; N, 12.22. $C_{29}H_{25}BN_4O$ requires C, 76.33; H, 5.52; N 12.28%]. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.81 (s, 3H), 3.67 (s, 3H), 6.57–6.60 (m, 2H), 7.19–7.21 (m, 2H), 7.23–7.32 (m, 9H), 7.41–7.43 (m, 4H), 7.50–7.51 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 40.2, 55.2, 111.4, 112.8, 117.2, 124.9, 126.9, 127.2, 127.6, 129.2, 130.6, 131.0, 133.7, 140.9, 144.0 (br), 158.6, 158.8.

*4.3.9. 5-Methyl-2,3,3-triphenyl-4H-1,2,4,3λ^4-triazaborine-6-carbonitrile (**3i**).* Recrystallization from cyclohexane/toluene mixture. Yield 0.88 g (50%), light orange crystals, mp 216.5–218.5 °C; [found: C, 75.17; H, 5.67; N, 15.72. $C_{22}H_{19}BN_4$ requires C, 75.45; H, 5.47; N 16.00]. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.21 (s, 3H), 7.09–7.11 (m, 3H), 7.18–7.27 (m, 6H), 7.33–7.39 (m, 6H), 8 (br s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 20.3, 110.5, 116.8, 122.9, 126.7, 127.3, 127.4, 127.8, 133.3, 145.9 (br), 146.6, 157.9.

*4.3.10. 5-Methyl-2-(4-dimethylaminophenyl)-3,3-diphenyl-4H-1,2,4,3λ^4-triazaborine-6-carbonitrile (**3j**).* Recrystallization from ethanol. Yield 0.60 g (30%), brown crystals, mp 193–195.5 °C; [found: C, 73.43; H, 6.39; N, 17.67. $C_{24}H_{24}BN_5$ requires C, 73.29; H, 6.15; N 17.81%]. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.15 (s, 3H), 2.83 (s, 6H), 6.31–6.33 (m, 2H), 7.07 (br s, 1H), 7.16–7.25 (m, 8H), 7.31–7.33 (m, 4H), ^{13}C NMR (125 MHz, $CDCl_3$): δ 20.3, 39.9, 109.1, 110.6, 117.5, 124.2, 126.6, 127.3, 133.3, 137.1, 146.5 (br), 149.5, 156.7.

*4.3.11. 2-(4-Methylphenyldiazenyl)-3-phenylaminobut-2-enenitrile (**5b**).* Recrystallization from cyclohexane. Yield 0.71 g (51%), yellow crystals, mp 139–141 °C; [found: C, 73.95; H, 5.91; N, 20.27. $C_{17}H_{16}N_4$ requires C, 73.89; H, 5.84; N 20.27%]. ^{1}H NMR (400 MHz, $CDCl_3$, 45 °C): δ 2.23 (s, 3H), 2.31 (s, 3H), 6.96–6.97 (br m, 2H), 7.12–7.14 (m, 2H), 7.21–7.23 (br m, 1H), 7.31–7.32 (br m, 2H), 7.37–7.41 (br m, 2H), 14.27 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, 45 °C): δ 18.21 (br), 20.77, 109.6 (br), 117.8 (br), 112.1 (br), 125.7 (br), 128.1, 129.1, 129.6, 136.6 (br), 143.3 (br), 160.9.

4.4. General procedure for synthesis of 4a and 4b

To a cold (5 °C) solution of 3-aminobut-2-enenitrile (**1a**) (0.41 g, 5 mmol) or 3-phenyl-3-aminoprop-2-enenitrile (**1c**) (0.72 g, 5 mmol) in dichloromethane (30 mL) was added water (0.3 mL) and diethylether (10 mL) and then freshly prepared corresponding benzenediazonium tetraphenylborate (5 mmol). The reaction mixture was stirred either 72 h at room temperature or 1.5 h at room temperature and then 3–4 h at reflux. The reaction mixture was cooled to room temperature and solvents were evaporated. The crude residue was chromatographed on silica gel with dichloromethane to give compounds **4a**–**c**.

*4.4.1. 6-Amino-4-methyl-5-(4-methylphenyldiazenyl)-2,2-diphenyl-3H-1,3,2λ^4-oxazaborine (**4a**).* Recrystallization from cyclohexane/toluene mixture. Yield 0.86 g (45%), yellow crystals, mp 215–217 °C; [found: C, 72.49; H, 6.31; N, 14.58. $C_{23}H_{23}BN_4O$ requires C, 72.27; H, 6.06; N 14.66%]. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.34 (s, 3H), 2.53 (s, 3H), 6.13 (s, 1H), 6.83 (s, 1H), 7.15–7.16 (m, 2H), 7.19–7.22 (m, 2H), 7.26–7.29 (m, 4H), 7.38–7.42 (m, 6H), 11.33 (br s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.1, 21.3, 114.4, 120.4, 126.4, 127.3, 129.5, 131.7, 137.5, 148.9 (br), 150.2, 161.9, 170.0.

*4.4.2. 6-Amino-5-(4-methoxyphenyldiazenyl)-4-methyl-2,2-diphenyl-3H-1,3,2λ^4-oxazaborine (**4b**).* Recrystallization from toluene. Yield 0.42 g (21%), yellow crystals, mp 180–183.5 °C; [found: C, 69.61; H, 5.88; N, 14.35. $C_{23}H_{23}BN_4O_2$ requires C, 69.36; H, 5.82; N 14.07%]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.54 (s, 3H), 3.81 (s, 3H), 6.14 (s, 1H), 6.80 (s, 1H), 7.21–7.25 (m, 2H), 7.27–7.30 (m, 4H), 7.40–7.42 (m, 4H), 7.48–7.51 (m, 2H), 11.25 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.3, 55.4, 114.0, 114.2, 121.8, 126.4, 127.3, 131.7, 146.4, 149.1 (br), 159.2, 161.9, 169.8.

*4.4.3. 6-Amino-5-(4-methylphenyldiazenyl)-2,2,4-triphenyl-3H-1,3,2λ^4-oxazaborine (**4c**).* The reaction proceeded with equimolar amount of enaminonitrile and undried diazonium salt in dichloromethane at room temperature (see Table 2). Recrystallization from toluene. Yield 0.53 g (24%), yellow crystals, mp 227–230 °C; [found: C, 75.73; H, 5.90; N, 12.54. $C_{28}H_{25}BN_4O$ requires C, 75.69; H, 5.67; N 12.61%]. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.31 (s, 3H), 6.38 (br d, 1H), 6.94 (br s, 1H), 7.09–7.10 (m, 2H), 7.22–7.25 (m, 4H), 7.29–7.32 (m, 4H), 7.46–7.50 (m, 6H), 7.52–7.54 (m, 1H), 7.61–7.63 (m, 2H), 11.58 (br s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.1, 114.4, 120.7, 126.5, 127.4, 128.0, 129.4, 129.5, 131.0, 131.8, 135.6, 137.7, 148.8 (br), 150.1, 163.6, 169.4.

4.5. 3-Amino-2-(4-methylphenyldiazenyl)but-2-enenitrile (5a) and (^{15}N-5a)

To a stirred solution of enaminonitrile **1a** (0.82 g, 10 mmol) in dichloromethane (70 mL) were added remelted sodium acetate (2.46 g, 30 mmol) and 4-methylbenzenediazonium tetrafluoroborate (2.06 g, 10 mmol) (^{15}N selectively labelled 4-methylbenzenediazonium tetrafluoroborate was prepared in the same manner as ^{15}N nonlabelled diazonium salt except that $Na^{15}NO_2$ (95% ^{15}N) was used). The reaction mixture was stirred at room temperature for 23 h. Then the reaction mixture was filtered and the filtrate was evaporated. The residue was crystallized from ethanol to give 1.32 g (66%) orange crystals. Mp 175–178 °C [Ref. 35 179 °C]. NMR for ^{15}N-**5a** (for notation see Scheme 4). ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.29 (s*, H4, maj. +H9 min.), 2.32 (s, H9, maj.), 2.45 (s, H4, min.), 7.19–7.23 (m, H7, maj. +H7, min.), 7.41–7.44 (m, H6, min.), 7.62–7.66 (m, H6, maj.), 8.04 (br s, NH min.), 8.31 (br s, NH maj.), 8.67 (br s, NH min+maj.). ^{13}C NMR (100 MHz, DMSO-d_6): δ 18.0 (d, $J_{C,N}$=2.8 Hz, C4, min.), 19.9 (C4, maj.), 21.3 (C9, min.), 21.4 (C9, maj.), 103.4 (C2, maj.), 104.3 (C2, min.), 114.9 (CN, min.), 116.7 (br, CN, maj.), 121.4 (d, $J_{C,N}$=4.1 Hz, C6, min.), 122.2 (d, $J_{C,N}$=4.1 Hz, C6, maj.), 130.0 (C7, maj.), 130.1 (C7, min.), 137.7 (C8, min.), 138.4 (C8, maj.),151.1 (d, $J_{C,N}$=5.3 Hz, C5, maj.), 151.3 (d, $J_{C,N}$=6.2 Hz, C5, min.), 164.6 (br s, C3, maj.), 168.4 (d, $J_{C,N}$=9.5 Hz, C3, min.). ^{15}N NMR (40, 55 MHz, DMSO-d_6): δ ($^{15}N_β$)=87.8 (maj.), 92.7 (min.).

*Although this signal belongs to both the isomers, this is singlet due to an accidental equivalence of the chemical shifts.

4.6. Preparation of 3a from 5a and diphenylborinic acid

To a stirred solution of azo coupling product **5a** (1 g, 5 mmol) in dichloromethane (35 mL) was added diphenylborinic acid (1 g, 5.5 mmol) (prepared according to Ref. 23). The reaction mixture was stirred at room temperature for 17 h. Dichloromethane was evaporated and the residue was chromatographed (silica gel/dichloromethane). The crude product was crystallized from toluene/cyclohexane to give 1 g (55%) yellow crystals. ^{1}H NMR data were in accordance with those obtained in Section 4.3.1.

4.7. Preparation of intermediate Im_b

All components were dried before use dichloromethane was stirred 2 days with P_2O_5 and then distilled, 3-aminobut-2-enenitrile was dried under vacuum for 14 h after recrystallization from toluene. The reaction proceeded under argon atmosphere. To a solution of β-enaminonitrile (**1a**) (0.74 g, 9 mmol) in dry dichloromethane (55 mL) freshly prepared 4-methylbenzenediazonium tetraphenylborate (3.95 g, 9 mmol) was added. The reaction mixture was stirred for 72 h at room temperature. The solid was filtered to give 1.93 g yellow crystals. MS (ESI neg): calcd for $[M-H]^-$ 441.2250, found for $C_{29}H_{27}BN_4$ *m*/*z* 441.2242. The filtrate was evaporated to dryness and the crude residue was chromatographed on silica gel with dichloromethane to give 0.74 g (23%) triazaborine **3a**.

Acknowledgements

The authors thank to Prof. Antonín Lyčka for his help with some NMR measurements. The work was financially supported by Ministry of Education, Youth and Sports of the Czech Republic (project MSM 002 162 7501).

Supplementary data

The table for comparison of intermediate's (**Im_b**) ^{13}C chemical shifts (Table S1). The crystallographic data (Table S2–S5). Supplementary data related to this article can be found online at doi:10.1016/j.tet.2011.12.082.

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